A STUDY TO ESTABLISH A DEGRADATION PROFILE FOR AZINPHOSMETHYL (GUTHION) ON APPLE FOLIAGE IN KERN COUNTY DURING JULY 1984

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SUMMARY

An apple orchard in Kern County was sampled for dislodgeable foliar pesticide residue after an application of azinphosmethyl. Samples were collected before application and at selected intervals post-application. The established reentry interval for azinphosmethyl on apples is 14 days. The residue level of 1.6 ug/cm^2 of azinphosmethyl and its oxon established through dermal dose-response testing on laboratory animals by Knaak, et. al. (1980 and 1982) and through controlled human testing by Richards, et. al. (1978) as negligibly hazardous, was not found to be exceeded at any time in this orchard during the study. Oxon levels also stayed at low levels except for a spike at 72 hours post-application. The existing reentry interval is adequate for worker safety given the conditions present in this orchard.

INTRODUCTION

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations. A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into the treated area. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a low-toxicity residue level. The adequacy of these safety intervals is under continual evaluation. This study was initiated to validate existing reentry intervals. The objective of this study was to monitor the foliar decay rates of the insecticide azinphosmethyl and to establish a degradation profile for the material.

Azinphosmethyl [0,0-Dimethyl S-<(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl> phosphorodithioate] is a Toxicity Category I organophosphate insecticide used extensively on tree crops. Azinphosmethyl (AZM) has an oral LD_{50}<rat> of 13 mg/kg and a dermal LD_{50}<rat> of 220 mg/kg (1). A common result of organophosphate poisoning is cholinesterase inhibition. A National Cancer Institute (NCI) carcinogenesis bioassay using mice gave negative results, while a bioassay with rats was indefinite (1).

Knaak and Iwata have calculated residue levels considered safe for AZM and its oxon. These values are 3.0 ug/cm^2 for the parent (thion) material and 0.05 ug/cm^2 for the major degradation product (oxon). These residue level values represent the maximum amount of residue material that can be present on foliage without concern as to possible hazard to unprotected workers. A residue level of 1.6 ug/cm^2 has been calculated as the safe level for AZM <u>and</u> its oxon. This study investigated the rate at which the residue levels declined to levels considered to be of low hazard toxicity.

METHODS AND MATERIALS

With assistance from the Kern County Agricultural Commissioner's office, cooperation was obtained from a grower using AZM on apples. The material used was Guthion 50W, EPA Reg.# 03125-00301 AA, registered by Mobay Chemical. The material was 50% active ingredient. The application rate in this study was 2 lbs/acre. The dilution rate was 166 gallons of water per acre. The reentry interval for this application was 14 days. The material was delivered by an FMC Speed Sprayer. The tank mix also contained Plictran (cyhexatin), an acaricide, and a buffer solution. The study site was a 13 acre apple orchard in southeast Kern County.

Within the sampled orchard three non-adjacent rows were selected for sampling. The rows ran from north to south. The first sampled row was on the southeastern quadrant of the orchard; the second row was near the center of the orchard; and, the third row was in the northwestern quadrant. This arrangement approximated a diagonal through the field. These rows were designated A, B and C, respectively. Each sampled row was marked at the beginning of the row and at the locations of the first and last trees sampled in the row. In Row A, sampling commenced on the 5th tree in from the south side. In Row B, sampling began on the 27th tree in from the south side and in Row C sampling began on the 5th tree in from the north side. In each row, a total of 8 trees were sampled, 4 on the left and 4 on the right. Each tree was sampled 2 times on the quadrants facing the entrance row. A total of 48 leaf discs (2 punches x 8 trees x 3 rows) were generated per sample set. Three replicate sample sets were taken during each sampling period. The leaves were selected in each tree quadrant at a height of 1.5 meters from the ground. Subsequent leaf punches were grouped as closely as possible.

Two days before application, pre-application samples were collected. Post-application samples were taken at 4 hours, 24 hours, 48 hours, 72 hours, 6 days, 7 days, 8 days, 9 days, and 14 days. An additional sample, collected during a day of harvest survey of Kern County, was taken on day 77 post-application.

Samples were taken using a 2.54 cm. diameter leaf punch. Each sample contained 48 leaf discs accumulated in four ounce glass jars. The leaf punch was cleaned with alcohol between row samplings. Sample jars were sealed with aluminum foil, capped and stored on ice. The ice was constantly replenished to insure temperature stability (0 to 5^{o}). All required protective equipment was worn during sampling.

Samples were shipped by common carrier to Chemistry Laboratory Serivces in Sacramento for analysis. Dislodgeable residues were removed by mechanically shaking the leaf discs in a water-surfactant solution. The aqueous wash was extracted with organic solvent, dried, concentrated or diluted as necessary, then analyzed by gas chromatography. Method sensitivity was 0.003 ug/cm^2. Weather conditions are summarized in Table Two and graphed in Figure Two.

RESULTS

The analytical results for AZM residue analysis are given in Table One. These results have been graphically displayed in Figure One.

DISCUSSION

Under the conditions of this study, the residue levels dropped rapidly within 6 days then tended to level off for the remaining period of the study. Even after 77 days had elapsed since application, detectable residues were still present, albeit at extremely low levels. At no time were parent compound levels (thions) above the level considered safe for worker reentry (3.0 ug/cm^2). However, at 72 hours post-application, a degradation product residue (oxon) was above the calculated safe level of 0.09 ug/cm^2. This occurred only once with subsequent samplings returning to non-detectable levels. This transient phenomenon may have been created when a relatively large amount of thion passed through into the oxon configuration during chemical degradation. By day 6, the combined residues AZM and its oxon were below 1.6 ug/cm^2. Oxon was also detected on the pre-application samples but none of these were over the low hazard residue level values. These were residues from earlier applications of material.

The role of weather in the degradation rate is not clear. The only conspicuous weather effect that may have had some impact on the degradation was the rain on Day 8 with an ensuing increase of the pesticide residue levels on Day 9. Whether this was caused by drip-down of foliage residues from the upper canopy to the lower sampled canopy, reversal of the degradation pathways, liberation of penetrated residues, random fluctuation or some other mechanism cannot be determined from this study.

Although low residue levels were reached very rapidly in this study, this data should not be construed as to justify the reduction of safety intervals at this time. The sample population of this study is insufficient for the data to be directly applied as a standard for degradation rates. This study only substantiates the existing safety interval as adequate, given the conditions of this apple orchard. Future studies incorporating more comprehensive weather monitoring capabilities and longer, more intensive foliage monitoring will be necessary before action can be considered to change safety intervals. However, there is no need to increase the safety interval, under the conditions that prevailed in the orchard studies.

REFERENCES

1) NIOSH: Registry of Toxic Effects of Chemical Substances (1982-1983)

2) Knaak, J.B. and Y. Iwata: The Safe Level Concept and the Rapid Field Method, Pesticide Residue and Exposure, ACS Symposium Series, pg. 23 (1982).

TABLE ONE

GUTHION RESIDUE DATA
(ug/cm^2)

DAY		REP A	REP B	REP C	AVG
Pre-application	thion(t)	0.38	0.38	0.51	0.42
	oxon (o)	0.03	0.028	0.047	0.035
Immediate post	(t)	2.7	2.15	2.5	2.45
	(o)	0.016	ND	ND	----
24 hour	(t)	1.6	2.11	2.03	1.91
	(o)	ND	ND	ND	ND
48 hour	(t)	1.95	1.78	2.03	1.92
	(o)	ND	ND	ND	ND
72 hour	(t)	2.27	2.38	1.7	2.12
	(o)	0.068	0.15	0.037	0.085
6 days	(t)	0.75	0.69	0.70	0.713
	(o)	ND	ND	ND	ND
7 days	(t)	0.69	0.65	0.71	0.683
	(o)	ND	ND	ND	ND
8 days	(t)	0.57	0.49	0.54	0.53
	(o)	ND	ND	ND	ND
14 days	(t)	0.43	0.54	0.69	0.55
	(o)	ND	ND	ND	ND
77 days	(t)	0.099	0.039	----	----

ND = None Detected (Minimum Detectable Level is 0.003 ug/cm^2).

TABLE TWO

JULY WEATHER DATA

DATE	TEMP F° HIGH	TEMP F° LOW	RAIN (inches)	WIND (mph)	REL. HUM (if avail)
9	86	62	---	NW18	---
10	91	55	---	NW12	---
11	91	63	---	NNW15	17%
12	94	54	.01	NW10	---
13	94	62	---	NW10	---
14	92	62	.04	SW7	---
15	91	69	---	NW9	---
16	88	64	.82	SW5	---
17	94	65	---	NW3	---
18	90	70	---	W10	---
19	82	65	---	NW11	---
20	84	65	---	NW14	---
21	84	63	---	NW7	---
22	77	58	---	NW8	---
23	81	56	---	S7	---
24	87	51	---	NW10	19%
25	78	53	---	NW10	---
26	94	53	---	NW12	---
27	90	60	---	NW12	---
28	85	58	.22	E8	---
29	85	53	.01	ESE10	---
30	89	58	---	W12	---
31	86	56	.05	NW5	---

46 1240

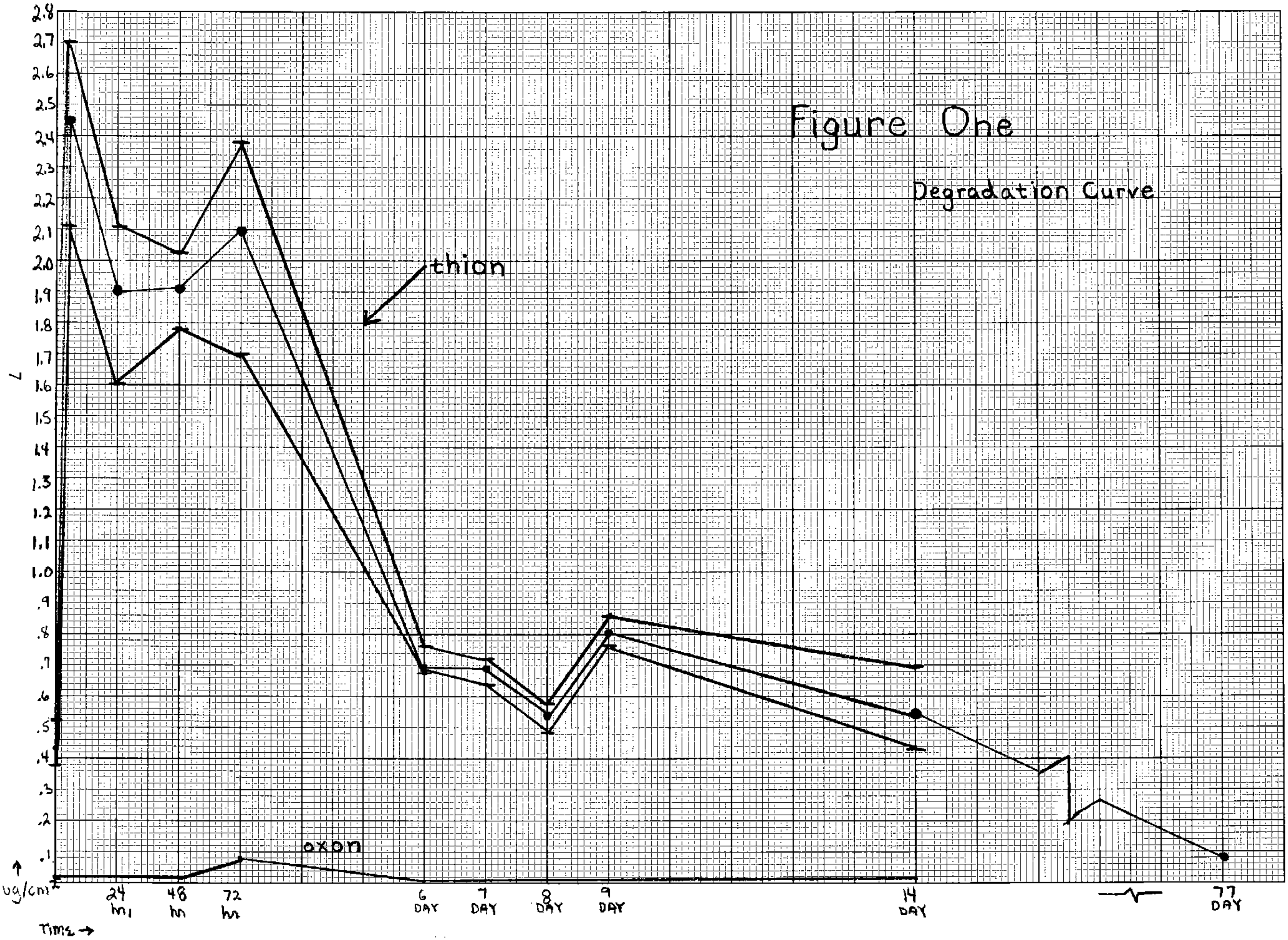
Figure One
Degradation Curve
thion
oxon
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
ug/cm²
24 hr
48 hr
72 hr
6 DAY
7 DAY
8 DAY
9 DAY
14 DAY
77 DAY
Time →

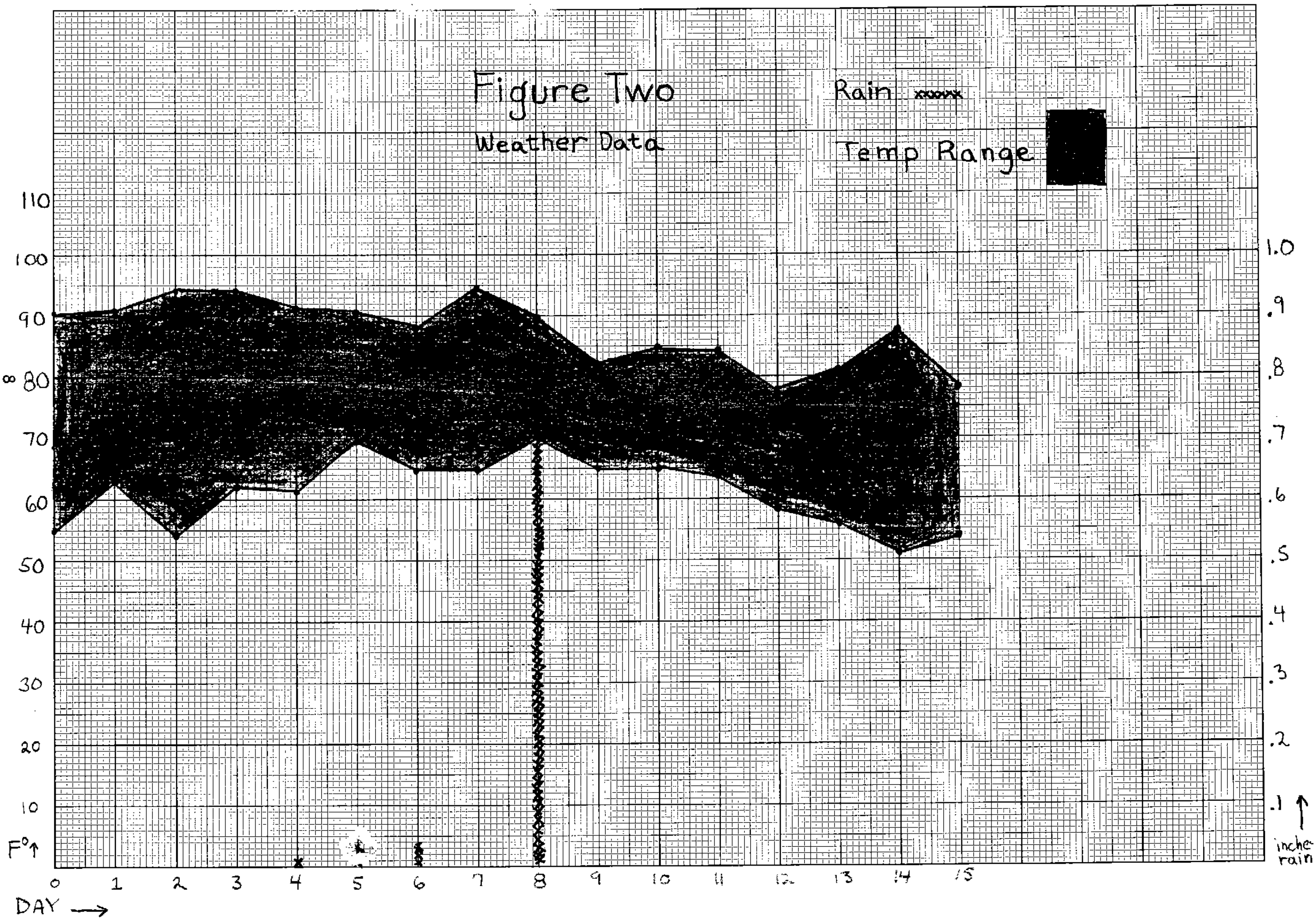
Figure Two
Weather Data
Rain xxxxx
Temp Range
110
100
90
80
70
60
50
40
30
20
10
F° ↑
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1 ↑
inche rain
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
DAY →